

Recovery of base metals from used fluid catalytic cracking (FCC) refining catalyst

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ABSTRACT

Base metals Zn, Fe, Cr and Mg were recovered from used (catalytic cracking) catalyst using sulfuric acid leaching method. After pre-treatment at 400°C for 4h, three sets of leaching fractions were carried out on the spent FCC catalyst. The residues were analyzed using FTIR and XRF techniques, while the leach liquors were analyzed using AAS technique to determine the concentrations of the leached metals present. Variable sulfuric acid concentrations of 0.5M, 1M and 2M; temperatures of 40, 60 and 80° and resident time (1h, 1.5h and 2h) were used. Optimum recovery was observed at heating temperature of 80°C, concentration of 2M and 2h leaching time.

Keywords: Base metals, FCC, Acid leaching, Optimum recovery, Used catalyst.

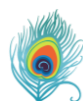
1. INTRODUCTION

By definition, a substance that participates in the reaction but not used up [1-3] and provides an alternative route with lower activation energy [4-7] is called catalyst. Industrial catalysts should be mechanically strong, selective, active, stable (to overheating), robust, easily be regenerated, and so forth [4-7].

The selection of catalysts for a certain process is made mainly out of technological and economic considerations. As opposed to precious metals, base metals are cheap, readily oxidizable metals with high susceptibility of corrosion [8]. In order to replace expensive catalysts, base metals are these days, widely used in heterogeneous catalysts as active components majorly in the forms of oxides, metals, nitrates etc. [9-12]

Mo-based heterogeneous catalysts are composed of metal oxides deposits, ranging from molybdenum and nickel oxide, nickel-molybdenum Ni-Mo catalysts; molybdenum and cobalt oxide, cobalt-molybdenum Co-Mo catalysts; tungsten and nickel oxide, nickel-tungsten Ni-W catalysts etc [6-7].

Numerous harmful effects are associated with used catalysts aside being extremely toxic to humans (carcinogenic, mutagenic) and the environment (highly mobile) if they get into the food chain or nature [6]. If the sulfur is not captured, it can cause acid rain or salt waste to contaminate surface and underground water [13-14, 25]. The heavy and light hydrocarbons can affect the air, the water and the soil if they are not treated. The toxicology of poisonous elements such as arsenic, selenium or fluoride in low concentration is well-known [13, 26].



Catalytic cracking process, developed for residue upgrading, commercialized later in 1930, was based on fixed bed technology upgraded later to fluidized bed catalytic cracking (FCC). The feed stock for catalytic cracking is normally light gas oil (LGO) from vacuum distillation unit. Catalytic cracking is employed to upgrade low value high molecular weight hydrocarbons to more value-added (low molecular weight) products like gasoline, LPG, diesel along with very important petrochemical feedstock like propylene, C₄ gases like isobutylene, Isobutane, butene and butane. [13]

Main reactions involved in catalytic cracking are: Cracking, isomerisation, dehydrogenation, hydrogen transfer, cyclization, condensation, alkylation and dealkylation. [14]

Base metals include metals such as, Nickel (Ni), Copper (Cu), Molybdenum (Mo), Cobalt (Co), Platinum (Pt), and Vanadium (V), are being increasingly used as lower-cost alternative catalyst materials. [15]

Disposal of these spent catalysts represent an increasing environmental problem due to their metallic content, being considered as hazardous waste [9-10]. Reusability and recycling of catalysts and catalytic materials ensures minimization of wastes, reduction in production costs, preservation of raw materials and environmental protection [3].

Although techniques are available in the literature concerning catalysts reactivation [2,5, 9,22], the extent of metal-recovery and efficiency of these methods is still lacking. Temperature programmed methods; TPD, TPO, TPR among others are commonly used to out-gas blocked catalysts [22].

Spent catalysts are generated in large quantities as solid waste on a yearly basis. To ensure compliance with environmental waste-disposal regulations and mitigate their hazardous nature, metals recovery from spent catalysts is very important [12].

The development of zeolite catalysts was a major breakthrough in the catalytic cracking process which demonstrated vastly superior activity, selectivity, and stability characteristics compared to original amorphous silica alumina catalyst [13]. Immense endeavor to develop breeds of high-matrix catalysts having cheaper accessibility, regenerability and robustness, high metal tolerance is still lacking [14-15].

Molybdenum (Mo), Cobalt (Co), Nickel (Ni) and Platinum (Pt) Catalysts

Due to the continued exploitation and exploration of world crude-oil supply and limited availability of low-sulfur crudes, metallic catalyst precursors are on the increase. Apart from their irreplaceable use in refining, they play immense role in ensuring safer environment through low sulfur emissions [9-10].

The most common oxide catalysts are those of oxides of Mo, Co (or Ni) on γ -alumina support [14]. According to [7, 9-10, 15] Mo-based catalysts are commonly composed of 10 - 30% Mo, 10 - 12% C, 8 - 12% S, 1 - 12% V, 1 - 6% Co, 0.5 - 6% Ni and the basis is γ -alumina. The Ni, Co and Mo-based catalysts are mostly prepared by soaking support solutions in which alumina is dissolved with salts of Mo, Co and Ni, after which the precursors are calcined at 600°C to obtain the oxides [6]. Mo oxides (MoO₃) presence in catalysts was verified in study by [9]. The Ni and Co oxides exercise a promoting effect on the activity of the catalytic system MoO₃-Al₂O₃ [9-10].

To get MoS₂, NiS and CoS in catalysts, Cibati [10] reported that an initial addition of H₂S gas is needed, where the active component is the MoS₂, activated by Co, which limits the sintering of the crystals.

Spent catalysts are important sources of Pt in addition to coke (C), vanadium (V), lead (Pb), nickel (Ni) etc. that may cause serious pollution to soil and water. As a consequence, they are classified as hazardous wastes with restricted disposal in landfills. Recovery of Pt from spent petroleum catalysts with the consideration of the environment is of great significance. Pt is the main active component of catalysts and disperses spontaneously on the surface of the supports. Although the content of Pt loading on the catalysts is only approximately 0.05–1.0 wt.%, it is the dominant attraction for recycling spent catalysts due to the high economic value.

These metals are used in the FCC catalysts due to their relative availability and inexpensiveness. The desire to provide an alternative or solution to recover these metals as a means to tackle scarcity, cost, the ever increasing demand for them and also to cripple their hazardous impact on the environment when disposed off as waste are the factors responsible for initiating this study.

Catalyst Deactivation; Poisoning; Fouling; Sintering/Phase Transformation

Activity of catalysts normally decreases with time [5,7,9,22]. The life of any catalyst generally depends on type of reactions as well as reaction conditions [5,22]. For example, catalysts for catalytic cracking lose much of their activity within seconds due to carbon deposition on the surface while promoted iron catalysts used in ammonia synthesis have a lifetime of years [4,7].

Poisoning basically involves chemisorption of reactants or products or feed impurities on the active sites of the catalyst surface, thereby decreasing the number of active sites available for catalytic reactions [22]. Since poisoning involves chemisorptions, it is known as chemical deactivation. This process can be reversible or irreversible. Compounds of sulphur and other materials are

frequently chemisorbed on nickel, copper and Pt catalysts [4,22].

In reversible poisoning, the strength of adsorption bond is not great and activity is regained when the poison is removed from the feed. When the adsorbed material is tightly held on the active sites, poisoning is irreversible and permanent [4,22].

Rapid deactivation can be caused by physical deposition of substance on the active sites of catalysts. Carbon deposition on catalysts used in petroleum industry falls in this category. Coke formation covers the active site of the catalysts and may also partially plug the pore entrance. This type of deactivation is partially reversible and regeneration can be done by burning in air [4,22].

Because of local high temperature, support of catalysts or catalyst itself may undergo structural modification or sintering causing a reduction in specific surface area or change in chemical nature of catalytic agent so that it becomes catalytically inactive. Hence, poisoning and fouling are dependent on concentration of reactant or product or impurities [4,22].

On the other hand, sintering and phase transformation may be assumed to be independent of fluid phase composition known as independent deactivation [4,22].

2. EXPERIMENTAL

Materials

Sample Procurement and Treatment

Spent FCC refining catalyst was obtained from Kaduna Refinery and Petrochemicals Company (KRPC), Kaduna State, Nigeria, Sulfuric Acid was purchased from Sigma Aldrich and stored until required for analyses.

Methods

Coke Elimination

Coke elimination was carried out using the method of Gerber *et al* [19] The spent refining catalyst (30g) was calcined by heating in a furnace at 400°C for 4h in order to eliminate coke deposits, physisorbed materials and improve solubility.

Preparation of Sulfuric Acid Solution (Leaching Agent)

Three sets of sulfuric acid solutions (0.5M, 1M and 1.5M) were prepared from sulfuric acid of analytical grade using distilled water. This is in accordance with the method reported by Gerber *et al.* [19].

Dissolution of Spent FCC Catalyst in Sulfuric Acid Solution

Three sets of leaching experiments were carried out in a round-bottomed flask, fitted with a reflux condenser and a magnetic stirrer, placed on a thermostatically controlled heating mantle.

First Batch of leachate solution contains spent FCC catalyst (2.0g) dissolved in 20ml of 0.5M H₂SO₄ solution at 40°C and stirring rate of 120rpm for 1h.

Second Batch of leachate solution contains spent FCC catalyst (2.0g) dissolved in 20ml of 1M H₂SO₄ solution at 60°C and stirring rate of 120rpm for 1.5h.

Third Batch of leachate solution contains spent FCC catalyst (2.0g) dissolved in 20ml of 2M H₂SO₄ solution at 80°C and stirring rate of 120rpm for 2h.

Product Analyses

At the end of the batch-leaching processes, the leaching solutions were suctioned out of the round bottom flask by a pipette, each of the leach liquor was cooled, filtered and analyzed for the concentration of metals using atomic absorption spectrometer (AAS).

Characterization

The residues from the three leachate filtrates were dried and characterized using XRF and FTIR techniques. Bulk scientific AAS model 210 was used for Atomic Absorption Spectroscopy (AAS) analysis. FTIR analysis was carried out using KBr disk method with the spectra recorded in the range of 4000-400 cm⁻¹.

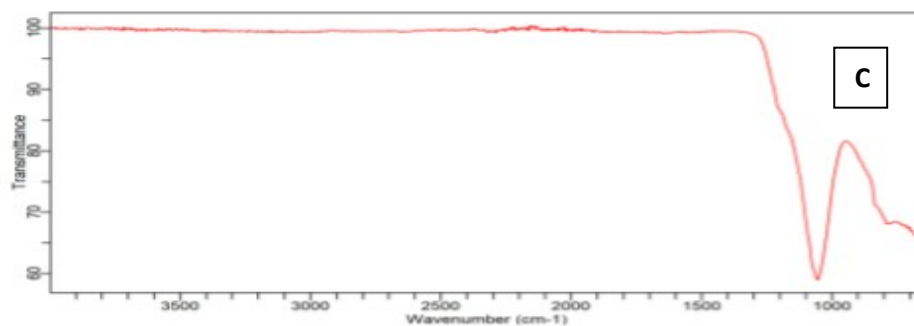
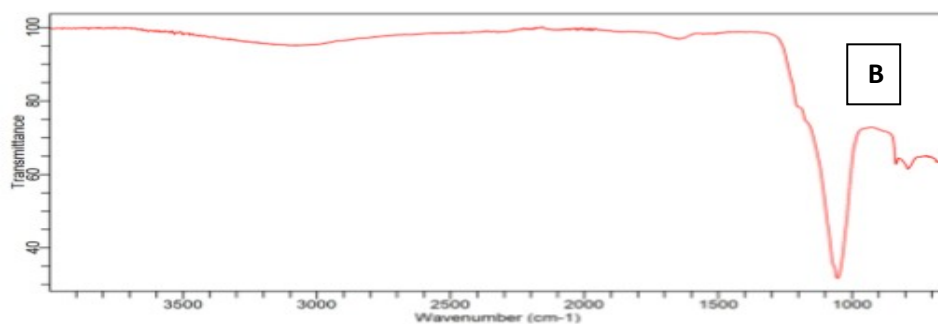
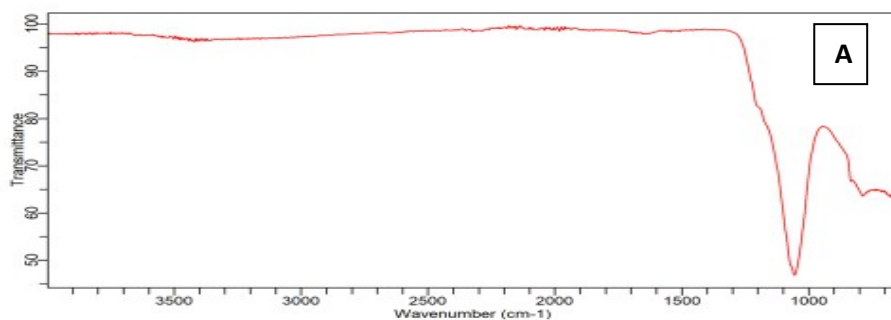
3. RESULTS

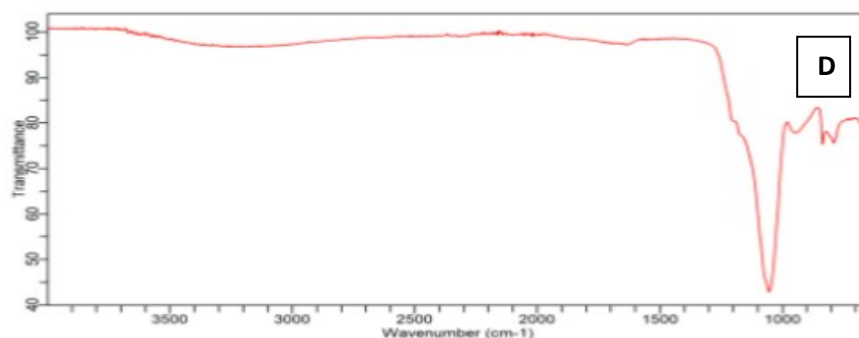
Result obtained in the various analytical techniques is presented in Tables 1-2 and figures A-D.

Table 1: XRF Results of Spent Catalyst and Leached Residues.

Elements (%)	Raw Catalyst	Leached Catalyst Residues		
		A*	B*	C*
Fe	0.65	0.61	0.43	0.10
Si	37.90	45.23	56.74	74.72
Al	36.42	33.93	25.87	10.12
Mg	0.63	0.52	0.52	0.28
P	0.59	0.44	0.46	0.52
S	0.08	0.48	1.64	1.93
Na	0.39	0.43	0.27	0.36
Ti	0.98	1.21	1.41	1.61
K	0.04	0.04	0.03	0.01
Cr	0.10	0.04	0.02	0.01

A*= 2.0g of spent catalyst, 20ml of 0.5M H₂SO₄, 40°C, 120rpm, 60 minutes; B*=2.0g of spent catalyst, 20ml of 1M H₂SO₄, 60°C, 120rpm, 90 minutes; C*=2.0g of spent catalyst, 20ml of 1.5M H₂SO₄, 80°C, 120rpm, 120 minutes.





Figures A-D: Showing FTIR Spectra of A(First Leachate), B (Second Leachate), C (Third Leachate) and D(Raw catalyst) under conditions stated beneath Table 1.

Table 2: AAS Results of the Leached Catalyst Filterates

Element (mg/L)	Leached Liquors		
	A	B	C
Zn	0.0387	0.0179	0.09157
Fe	1.1671	1.6332	2.6717
Cr	0.1417	0.1617	0.1818
Mg	59.2056	64.8708	61.5539

4. DISCUSSION

The XRF results (Table 1) clearly showed variations in the elemental concentrations of recovered solids as compared with that of the raw unleached sample. It is clear that the concentrations of Fe, Al, Mg, P, K and Cr gradually decrease across the series of leaching tests conducted. Thus, these means that sulfuric acid was to an extent, effective in the extraction of the above elements mentioned.

Si, S and Ti (Table 1) appear to be increasing with lower concentrations in the raw (unleached) sample and the highest in the third catalyst residue (C). On the other hand, the concentration of Fe, Al, Mg, Na, K and Cr metals is observed to show an opposite pattern with decrease in leached samples across A-C.

Table 2 presents the AAS results clearly show some variations in the elemental concentration of recovered metals (Zn, Fe, Cr and Mg) solubilized in the leach liquor by the leachate.

It is obvious that the recovery of Zn occurred best at the conditions of temperature (80°C), leaching agent concentration (2M) and leaching time of 2h. The above factors also hold for the recovery of Fe and Cr.

Accordingly, the best recovery rate of Mg was observed at conditions of temperature (60°C), leaching agent concentration (1M) and leaching time of 1h. The best recovery for these metals occur at the variable conditions of temperature (80°C), leaching agent concentration (2M) and leaching time of 2 h.

Figures A-D show the FTIR spectra of the residue after the first leached sample. The spectrum (A) shows appearance of clay mineral bond around 950cm⁻¹ which suggests a strong evidence of Si-O group. Other available bonds include; S=O (sulfoxide group) at 1050 cm⁻¹ and C=C group at 800 cm⁻¹. Spectra B shows the infrared spectrum of the residue after the second leaching process. The spectrum shows a strong bond at 1050 cm⁻¹ which indicates the presence of S=O group and also C=C group at 800-900 cm⁻¹. Spectra C shows the infrared spectrum of the residue after the third leaching process. The spectrum shows a strong bond at 1050 cm⁻¹ which indicates the presence of S=O (sulfoxide group). There is also the occurrence of C=C groups at both 1000, 900 and 850 cm⁻¹. Spectra D shows the infrared spectrum of the raw spent FCC catalyst itself. The spectrum shows strong band at 1050 cm⁻¹ which indicates the presence of S=O (sulfoxide group) and also C=C group at 950cm⁻¹. It is seen that the spectrum are quite similar.

This is as a result of the fact that they all have same constituents and the little variations in leaching factors, supported by the XRF results.

Effect of Sulfuric Acid Concentration

It has been outlined that the leaching fractions A, B and C were carried out using different concentrations of sulfuric acid solutions. 0.5M, 1M and 2M H₂SO₄ solutions were used for leaching solutions A, B and C respectively. The percentage sulfur composition in the leached residues increased gradually from 0.48 in leachate A, to 1.64 and further to 1.93 in B and C leachates with time respectively. This clearly indicates that variation in sulfuric acid concentration has significance in the recovery process.

Effect of Temperature Variation

The leaching fractions (A, B and C) were obtained at 40, 60 and 80°C respectively. There is an observable decrease in the concentration of Fe, Al, Mg, K and Cr. Reports by [5, 9] confirm that temperature plays a vital role in the activation and deactivation of catalysts. Accordingly, the results in Table 1 shows gradual decrease in the metal concentrations.

Effect of Contact Time

Leached residues in A, B and C were soaked in sulfuric acid solutions for 60, 90 and 120 minutes respectively. Table 1 presents the percentage composition of the available elements in the variable fractions. Generally, the period for which the reactants collide and their moles available are amongst factors reported to have effect on the leaching ability [7]. It is clear that there is a general decrease from A-C in all the percentage compositions with time, with the exception of S, Ti and Si which increased with time. At 60 minutes leaching time (A), composition of Fe (0.61) was higher than 0.43 and 0.10 in B and C leached residues respectively.

5. CONCLUSION

Sulphuric acid leaching process carried out in the recovery process for the FCC catalyst at hand proved effective. Variation in concentration, contact time and temperature of reaction as reported by [19] play a key role in metal recovery from spent catalysts.

Further work

The further work will include comparison of surface properties of used versus fresh FCC catalyst, determination of reusability of the used catalyst through surface and active composition modifications.

Conflict of interest

The authors declare that they have no conflict of interest.

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Ethical approval

This article does not contain any studies with human participants performed by any of the authors.

Data and materials availability:

All data associated with this study are present in the paper.

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